Equation satisfied by electron-electron mutual Coulomb repulsion energy density functional.

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It is shown that the electron-electron mutual Coulomb repulsion energy density functional $V_{ee}^{\gamma}[\rho]$ satisfies the equation

$$V_{ee}^{\gamma}\left[\rho_N^1\right] - V_{ee}^{\gamma}\left[\rho_{N-1}^{\gamma}\right]$$
$$= \int d^3r \frac{\delta V_{ee}^{\gamma}\left[\rho_N^1\right]}{\delta \rho_N^1(\mathbf{r})}\left(\rho_N^1(\mathbf{r}) - \rho_{N-1}^{\gamma}(\mathbf{r})\right)$$

where $\rho_N^1(\mathbf{r})$ and $\rho_{N-1}^{\gamma}(\mathbf{r})$ are N-electron and $(N-1)$-electron densities determined from the same adiabatic scaled external potential of the N-electron system at coupling strength γ.

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I. INTRODUCTION

Density Functional Theory (DFT)[1] is one of the most important tools for the calculation of electronic structure and structural properties of solids and molecules[2]. In all practical applications approximations are used[2]. It is therefore important to examine the exact formal properties of functionals that enter into the formalism as an aid to understanding the underlying formulation and to develop improved approximations. Here the Coulomb interaction energy functional

$$V_{ee}^{\gamma}\left[\rho_N^{\gamma}\right] = \left\langle \Psi_{\rho_N^{\gamma}}^{\gamma} \left| \hat{V}_{ee} \right| \Psi_{\rho_N^{\gamma}}^{\gamma} \right\rangle \tag{1}$$

is examined. $\left| \Psi_{\rho_N^{\gamma}}^{\gamma} \right\rangle$ is the N-electron wavefunction that yields the density ρ_N^{γ} and minimizes $\left\langle \Psi \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi \right\rangle$[3]:

$$\min_{\Psi \to \rho_N^{\gamma}} \left\langle \Psi \left| \hat{T} + \gamma \hat{V}_{ee} \right| \Psi \right\rangle = \left\langle \Psi_{\rho_N^{\gamma}}^{\gamma} \left| \hat{V}_{ee} \right| \Psi_{\rho_N^{\gamma}}^{\gamma} \right\rangle. \tag{2}$$

$\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and electron-electron repulsion operators respectively and γ scales the electron-electron interaction energy. In this paper it is shown that

$$V_{ee}^{\gamma}\left[\rho_N^1\right] - V_{ee}^{\gamma}\left[\rho_{N-1}^{\gamma}\right]$$
$$= \int d^3r \frac{\delta V_{ee}^{\gamma}\left[\rho_N^1\right]}{\delta \rho_N^1\left(\mathbf{r}\right)} \left(\rho_N^1\left(\mathbf{r}\right) - \rho_{N-1}^{\gamma}\left(\mathbf{r}\right)\right). \tag{3}$$

where $\rho_N^1\left(\mathbf{r}\right)$ and $\rho_{N-1}^{\gamma}\left(\mathbf{r}\right)$ are N-electron and $(N-1)$-electron densities determined from the same external adiabatic potential at coupling strength γ as discussed below. As a corollary it will be shown that

$$V_{ee}^{\gamma}\left[\rho_N^1\right] = \sum_{L=0}^{N-2} \int d^3r \frac{\delta V_{ee}^{\gamma}\left[\rho_{N-L}^{\gamma}\right]}{\delta \rho_{N-L}^{\gamma}\left(\mathbf{r}\right)} \left(\rho_{N-L}^{\gamma}\left(\mathbf{r}\right) - \rho_{N-1-L}^{\gamma}\left(\mathbf{r}\right)\right). \tag{4}$$

II. PROOF

In the adiabatic connection approach[4–7] of the constrained minimization formulation of density functional theory[1,3,8,9] the Hamiltonian $\hat{H}^{\gamma}$ for a system of N electrons is given by

$$\hat{H}_N^{\gamma} = \hat{T}^N + \gamma \hat{V}_{ee}^N + \hat{v}_{N,\text{ext}}^{\gamma}\left[\rho_N\right]. \tag{5}$$

Atomic units, $\hbar = e = m = 1$ are used throughout. $\hat{T}$ is the kinetic energy operator,

$$\hat{T}^N = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \tag{6}$$

and $\gamma\hat{V}_{ee}$ is a scaled electron-electron interaction,

$$\gamma\hat{V}_{ee}^N = \gamma\sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{7}$$

The the external potential

$$\hat{v}_{N,\text{ext}}^{\gamma}[\rho_N] = \sum_{i=1}^{N} v_{\text{ext}}^{\gamma}\left([\rho_N];\mathbf{r}_i\right), \tag{8}$$

is constructed to keep the charge density fixed at $\rho_N(\mathbf{r})$, the ground state charge density of the fully interacting system ($\gamma = 1$), for all values of the coupling constant γ. The external potential has the form[9,10]

$$v_{\text{ext}}^{\gamma}\left([\rho_N];\mathbf{r}\right) = (1-\gamma)\, v_{ux}([\rho_N];\mathbf{r})$$
$$+ v_c^1([\rho_N];\mathbf{r}) - v_c^{\gamma}([\rho_N];\mathbf{r}) + v_{\text{ext}}^1([\rho_N];\mathbf{r}), \tag{9}$$

where $v_{\text{ext}}^1([\rho_N];\mathbf{r}) = v_{\text{ext}}(\mathbf{r})$ is the external potential at full coupling strength, $\gamma = 1$, and $v_{\text{ext}}^0([\rho_N];\mathbf{r})$ is non-interacting Kohn-Sham potential. The exchange plus Hartree potential[11,12] $v_{ux}([\rho_N];\mathbf{r})$, is independent of γ, while the correlation potential $v_c^{\gamma}([\rho_N];\mathbf{r})$ depends in the scaling parameter γ.

The chemical potential

$$\mu_N = E_N^{\gamma}\left(v_{\text{ext}}^{\gamma}[\rho_N]\right) - E_{N-1}^{\gamma}\left(v_{\text{ext}}^{\gamma}[\rho_N]\right) \tag{10}$$

depends on the asymptotic decay of the charge density[11–13], and hence is independent of the coupling constant γ[14,15]. In Eq. (10) E_{N-1}^{γ} is the groundstate energy of the $(N-1)$-electron system with the same single-particle external potential $v_{\text{ext}}^{\gamma}([\rho_N];\mathbf{r})$ as the N-electron system:

$$\hat{H}_{N-1}^{\gamma}\left|\Psi_{\rho_{N-1}^{\gamma}}^{\gamma}\right\rangle = E_{N-1}^{\gamma}\left|\Psi_{\rho_{N-1}^{\gamma}}^{\gamma}\right\rangle$$
$$\hat{H}_{N-1}^{\gamma} = \hat{T}^{N-1} + \gamma\hat{V}_{ee}^{N-1} + \hat{v}_{N-1,\text{ext}}^{\gamma}[\rho_N]$$
$$\hat{v}_{N-1,\text{ext}}^{\gamma}[\rho_N] = \sum_{i=1}^{N-1} v_{\text{ext}}^{\gamma}\left([\rho_N];\mathbf{r}_i\right) \tag{11}$$

Note that by construction of $v_{\text{ext}}^{\gamma}\left(\left[\rho_N\right];\mathbf{r}\right)$, Eq. (9) $\rho_N = \rho_N^1$ is independent of γ, but the groundstate density of the $(N-1)$-electron system ρ_{N-1}^{γ}, is a function of γ.

The correlation energy $E_c^{\gamma}\left[\rho_{N-1}^{\gamma}\right]$ is defined as[9]

$$E_c^{\gamma}\left[\rho_{N-1}^{\gamma}\right] = \left\langle \Psi_{\rho_{N-1}^{\gamma}}^{\gamma} \left| \hat{T}^{N-1} + \gamma \hat{V}_{ee}^{N-1} \right| \Psi_{\rho_{N-1}^{\gamma}}^{\gamma} \right\rangle \\ - \left\langle \Psi_{\rho_{N-1}^{\gamma}}^0 \left| \hat{T}^{N-1} + \gamma \hat{V}_{ee}^{N-1} \right| \Psi_{\rho_{N-1}^{\gamma}}^0 \right\rangle, \tag{12}$$

where $\left| \Psi_{\rho_{N-1}^{\gamma}}^0 \right\rangle$ is the Kohn-Sham $(N-1)$ independent particle groundstate wavefunction that yields the same density as the interacting $(N-1)$-electron system at coupling strength γ. The correlation part of the kinetic energy is given by

$$T_c^{\gamma}\left[\rho_{N-1}^{\gamma}\right] = \left\langle \Psi_{\rho_{N-1}^{\gamma}}^{\gamma} \left| \hat{T}^{N-1} \right| \Psi_{\rho_{N-1}^{\gamma}}^{\gamma} \right\rangle \\ - \left\langle \Psi_{\rho_{N-1}^{\gamma}}^0 \left| \hat{T}^{N-1} \right| \Psi_{\rho_{N-1}^{\gamma}}^0 \right\rangle. \tag{13}$$

The virial theorem can be written as[9]

$$2T^{\gamma}\left[\rho\right] + \gamma V_{ee} + \int d^3r' v^{\gamma}\left(\left[\rho\right];\mathbf{r}'\right)\left(3\rho\left(\mathbf{r}'\right) + \mathbf{r}'.\nabla'\rho\left(\mathbf{r}'\right)\right) = 0 \tag{14}$$

or as

$$T^{\gamma}\left[\rho\right] + F^{\gamma}\left[\rho\right] + \int d^3r' v^{\gamma}\left(\left[\rho\right];\mathbf{r}'\right)\left(3\rho\left(\mathbf{r}'\right) + \mathbf{r}'.\nabla'\rho\left(\mathbf{r}'\right)\right) = 0 \tag{15}$$

where the energy functional $F^{\gamma}\left[\rho\right]$ is given by[11,12]

$$F^{\gamma}\left[\rho\right] = T^{\gamma}\left[\rho\right] + \gamma V_{ee}^{\gamma}\left[\rho\right] \\ = T^0\left[\rho\right] + \gamma\left(E_x\left[\rho\right] + U\left[\rho\right]\right) + E_c^{\gamma}\left[\rho\right] \tag{16}$$

$T^{\gamma}\left[\rho\right]$ and $E_c^{\gamma}\left[\rho\right]$ are the kinetic and correlation energies for the interacting system at coupling strength γ and density ρ while $E_x\left[\rho\right]$ and $U\left[\rho\right]$ are the exchange and Hartree energies at ρ.

Take the functional derivative of Eq. (15) with respect to $v^{\gamma}\left(\mathbf{r}''\right) = v_{\text{ext}}^{\gamma}\left(\left[\rho\right];\mathbf{r}''\right)$ and use the chain rule for functional derivatives (here and in the following the assumption is made that all the functional derivatives are well defined[16]):

$$0 = \int d^3r' \frac{\delta T^{\gamma}\left[\rho\right]}{\delta\rho\left(\mathbf{r}'\right)} \left.\frac{\delta\rho\left(\mathbf{r}'\right)}{\delta v^{\gamma}\left(\mathbf{r}''\right)}\right|_N + \int d^3r' \frac{\delta F^{\gamma}\left[\rho\right]}{\delta\rho\left(\mathbf{r}'\right)} \left.\frac{\delta\rho\left(\mathbf{r}'\right)}{\delta v^{\gamma}\left(\mathbf{r}''\right)}\right|_N + 3\rho\left(\mathbf{r}''\right) + \mathbf{r}''.\nabla''\rho\left(\mathbf{r}''\right) \\ - \int d^3r' \mathbf{r}'.\nabla' v^{\gamma}\left(\left[\rho\right];\mathbf{r}'\right) \left.\frac{\delta\rho\left(\mathbf{r}'\right)}{\delta v^{\gamma}\left(\mathbf{r}''\right)}\right|_N. \tag{17}$$

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The subscript N in $\left.\frac{\delta\rho(\mathbf{r}')}{\delta v^\gamma(\mathbf{r}'')}\right|_N$ indicates that the functional derivative is taken at constant particle number. A useful expression is the Berkowitz-Parr equation[17,18] which states that

$$\left.\frac{\delta\rho\left(\mathbf{r}'\right)}{\delta v^\gamma\left(\mathbf{r}\right)}\right|_N = \left(-s^\gamma\left(\mathbf{r}',\mathbf{r}\right) + \frac{s^\gamma\left(\mathbf{r}'\right)s^\gamma\left(\mathbf{r}\right)}{S^\gamma}\right), \tag{18}$$

where

$$s^\gamma\left(\mathbf{r}',\mathbf{r}\right) = \left(\frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}'\right)\delta\rho\left(\mathbf{r}\right)}\right)^{-1}, \tag{19}$$

$$s^\gamma\left(\mathbf{r}\right) = \int d^3r s^\gamma\left(\mathbf{r},\mathbf{r}'\right) \tag{20}$$

and

$$S^\gamma = \frac{1}{\eta^\gamma} \tag{21}$$

where

$$\eta^\gamma = \left.\frac{\partial\mu}{\partial N}\right|_{v^\gamma} \tag{22}$$

and μ is the chemical potential, independent of γ[14,15]. In addition

$$s^\gamma\left(\mathbf{r}\right) = S^\gamma f^\gamma\left(\mathbf{r}\right) \tag{23}$$

where the Fukui function[17,18]

$$f^\gamma\left(\mathbf{r}\right) = \left.\frac{\delta\mu}{\delta\rho\left(\mathbf{r}\right)}\right|_N = \left.\frac{\delta\rho\left(\mathbf{r}\right)}{\delta N}\right|_{v^\gamma} \tag{24}$$

satisfy

$$\int d^3r' \frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}\right)\delta\rho\left(\mathbf{r}'\right)} f^\gamma\left(\mathbf{r}'\right) = \eta^\gamma, \tag{25}$$

where η^γ is a constant.

Multiply (17) by $\frac{\delta^2 F^\gamma[\rho]}{\delta\rho(\mathbf{r}'')\delta\rho(\mathbf{r})}$ and integrate over $\mathbf{r}''$. With (18) and (19) the result is

$$\begin{aligned}
0 = &-\frac{\delta T^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}\right)} - \frac{\delta F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}\right)} + \mathbf{r}.\nabla v^\gamma\left(\left[\rho\right];\mathbf{r}\right) \\
&+ \int d^3r'' \int d^3r' \frac{\delta T^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}'\right)} \frac{s^\gamma\left(\mathbf{r}'\right)s^\gamma\left(\mathbf{r}''\right)}{S^\gamma} \frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}''\right)\delta\rho\left(\mathbf{r}\right)} \\
&+ \int d^3r'' \int d^3r' \frac{\delta F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}'\right)} \frac{s^\gamma\left(\mathbf{r}'\right)s^\gamma\left(\mathbf{r}''\right)}{S^\gamma} \frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}''\right)\delta\rho\left(\mathbf{r}\right)} \\
&- \int d^3r''' \int d^3r' \int d^3r' \mathbf{r}'.\nabla'v^\gamma\left(\left[\rho\right];\mathbf{r}'\right) \frac{s^\gamma\left(\mathbf{r}'\right)s^\gamma\left(\mathbf{r}''\right)}{S^\gamma} \frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}''\right)\delta\rho\left(\mathbf{r}\right)} \\
&+ \int d^3r' \left(3\rho\left(\mathbf{r}''\right) + \mathbf{r}''.\nabla''\rho\left(\mathbf{r}''\right)\right) \frac{\delta^2 F^\gamma\left[\rho\right]}{\delta\rho\left(\mathbf{r}''\right)\delta\rho\left(\mathbf{r}\right)}
\end{aligned} \tag{26}$$

Since $\frac{\delta^2 F^\gamma[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}$ is symmetric in $\mathbf{r}$ and $\mathbf{r}'$, Eq. (26), with the relations (23) and (25) becomes

$$
\begin{aligned}
0 = & -\frac{\delta T^\gamma[\rho]}{\delta\rho(\mathbf{r})} - \frac{\delta F^\gamma[\rho]}{\delta\rho(\mathbf{r})} + \mathbf{r}.\nabla v^\gamma([\rho];\mathbf{r}) \\
& + \int d^3 r' \frac{\delta T^\gamma[\rho]}{\delta\rho(\mathbf{r}')} f^\gamma(\mathbf{r}') \\
& + \int d^3 r' \frac{\delta F^\gamma[\rho]}{\delta\rho(\mathbf{r}')} f^\gamma(\mathbf{r}') - \int d^3 r' \mathbf{r}'.\nabla'' v^\gamma([\rho];\mathbf{r}') f^\gamma(\mathbf{r}') \\
& + \int d^3 r' (3\rho(\mathbf{r}'') + \mathbf{r}''.\nabla''\rho(\mathbf{r}'')) \frac{\delta^2 F^\gamma[\rho]}{\delta\rho(\mathbf{r}'')\delta\rho(\mathbf{r})}.
\end{aligned} \tag{27}
$$

Since[11]

$$
\begin{aligned}
\frac{d}{d\lambda} & \frac{\delta G[\rho_\lambda]}{\delta\rho_\lambda(\mathbf{r})} \\
& = \int d^3 r'' \frac{\delta G[\rho_\lambda]}{\delta\rho_\lambda(\mathbf{r})\delta\rho_\lambda(\mathbf{r}'')} \frac{d}{d\lambda}\rho_\lambda(\mathbf{r}''),
\end{aligned} \tag{28}
$$

it follows that if $\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$, the uniformly scaled density,

$$
\frac{d}{d\lambda} \left.\frac{\delta F^\gamma[\rho_\lambda]}{\delta\rho_\lambda(\mathbf{r})}\right|_{\rho_\lambda,\lambda=1} = \int d^3 r' (3\rho(\mathbf{r}') + \mathbf{r}'.\nabla\rho(\mathbf{r}')) \frac{\delta^2 F^\gamma[\rho]}{\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r})}. \tag{29}
$$

Now consider the Schrödinger equation

$$
\begin{aligned}
& \left[-\frac{1}{2}\sum_{i=1}^N \nabla_i^2 + \frac{\gamma}{\lambda}\sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v^{\frac{\gamma}{\lambda}}([\rho];\mathbf{r}_i) \right] \Psi^{\frac{\gamma}{\lambda}}(\{\mathbf{r}_i\}) \\
& = E\left(v^{\frac{\gamma}{\lambda}}[\rho] \right) \Psi^{\frac{\gamma}{\lambda}}(\{\mathbf{r}_i\})
\end{aligned} \tag{30}
$$

from which it follows that

$$
\begin{aligned}
& \left[-\frac{1}{2}\sum_{i=1}^N \nabla_i^2 + \gamma\sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \lambda^2 v^{\frac{\gamma}{\lambda}}([\rho];\mathbf{r}_i) \right] \Psi^{\frac{\gamma}{\lambda}}(\{\lambda\mathbf{r}_i\}) \\
& = \lambda^2 E\left(v^{\frac{\gamma}{\lambda}}[\rho] \right) \Psi^{\frac{\gamma}{\lambda}}(\{\lambda\mathbf{r}_i\}).
\end{aligned} \tag{31}
$$

The Levy constrained minimization approach[3] implies that $\Psi^{\frac{\gamma}{\lambda}}(\{\lambda\mathbf{r}_i\})$ yields $\lambda^3\rho(\lambda\mathbf{r})$ and minimizes $\left\langle \Psi \left| \hat{T} + \gamma\hat{V}_{ee} \right| \Psi \right\rangle_{\Psi\to\lambda^3\rho(\lambda\mathbf{r})}$. Therefore[9,11–13]

$$
\frac{\delta F^\gamma[\rho_\lambda]}{\delta\rho_\lambda(\mathbf{r})} + \lambda^2 v^{\frac{\gamma}{\lambda}}([\rho];\lambda\mathbf{r}) = \mu_\lambda^\gamma. \tag{32}
$$

where, for an N-electron system

$$
\mu_{N,\lambda}^\gamma = E_N^\gamma\left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N] \right) - E_{N-1}^\gamma\left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N] \right) \tag{33}
$$

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with $E_N^\gamma \left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N]\right)$ and $E_{N-1}^\gamma \left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N]\right)$ the groundstate energies of the N and $(N-1)$ electron systems with the same external potential $\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N]$. From Eq.(31) it follows that

$$
\begin{aligned}
\mu_{N,\lambda}^\gamma &= E_N^\gamma \left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N]\right) - E_{N-1}^\gamma \left(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N]\right) \\
&= \lambda^2 \left(E_N^\gamma \left(v^{\frac{\gamma}{\lambda}}[\rho_N]\right) - E_{N-1}^\gamma \left(v^{\frac{\gamma}{\lambda}}[\rho_N]\right) \right) \\
&= \lambda^2 \mu_N
\end{aligned}
\tag{34}
$$

where the last step follows from Eq. (10). The chemical potential μ_N is independent of γ[14,15].
Combining (9), (29), (32) and (34) yields (suppressing the subscript N for convenience)

$$
\int d^3 r' \left(3\rho\left(\mathbf{r}''\right) + \mathbf{r}''.\nabla\rho\left(\mathbf{r}''\right)\right) \frac{\delta^2 F^\gamma [\rho]}{\delta\rho\left(\mathbf{r}''\right)\delta\rho\left(\mathbf{r}\right)}
$$
$$
= 2\mu - 2v^\gamma \left([\rho];\mathbf{r}\right) - \mathbf{r}.\nabla v^\gamma \left([\rho];\mathbf{r}\right) - \left(\gamma v_x \left([\rho];\mathbf{r}\right) + \gamma u \left([\rho];\mathbf{r}\right) + \gamma\frac{d}{d\gamma}v^\gamma \left([\rho];\mathbf{r}\right)\right). \tag{35}
$$

Upon substitution of (35) into (27),

$$
\frac{\delta T^\gamma [\rho]}{\delta\rho\left(\mathbf{r}\right)} + \frac{\delta F^\gamma [\rho]}{\delta\rho\left(\mathbf{r}\right)} + 2v^\gamma \left([\rho];\mathbf{r}\right) + \left(\gamma v_x \left([\rho];\mathbf{r}\right) + \gamma u_x \left([\rho];\mathbf{r}\right) + \gamma\frac{d}{d\gamma}v^\gamma \left([\rho];\mathbf{r}\right)\right)
$$
$$
= \int d^3 r' \frac{\delta T^\gamma [\rho]}{\delta\rho\left(\mathbf{r}'\right)} f^\gamma \left(\mathbf{r}'\right) + \int d^3 r' \frac{\delta F^\gamma [\rho]}{\delta\rho\left(\mathbf{r}'\right)} f^\gamma \left(\mathbf{r}'\right) - \int d^3 r'' \int d^3 r' \mathbf{r}'.\nabla'v^\gamma \left(\mathbf{r}'\right) f^\gamma \left(\mathbf{r}'\right) + 2\mu \tag{36}
$$

With the aid of (32), (16) and (9)

$$
\frac{\delta T_c^\gamma [\rho]}{\delta\rho\left(\mathbf{r}\right)} + \gamma\frac{d}{d\gamma}v_c^\gamma \left([\rho];\mathbf{r}\right) - v_c^\gamma \left([\rho];\mathbf{r}\right) - 2\mu
$$
$$
= -\int d^3 r' \frac{\delta V_{ee}^\gamma [\rho]}{\delta\rho\left(\mathbf{r}'\right)} f^\gamma \left(\mathbf{r}'\right) - 2\int d^3 r' v^\gamma \left([\rho];\mathbf{r}'\right) f^\gamma \left(\mathbf{r}'\right) - \int d^3 r' \mathbf{r}'.\nabla'v^\gamma \left([\rho];\mathbf{r}'\right) f^\gamma \left(\mathbf{r}'\right) \tag{37}
$$

where

$$
T_c^\gamma [\rho] = T^\gamma [\rho] - T^0 [\rho]. \tag{38}
$$

From the definition of $E_c^\gamma [\rho]$ and $T_c^\gamma [\rho]$[9,11–13], Eqs. (12) and (13) it follows that

$$
\frac{\delta T_c^\gamma [\rho]}{\delta\rho\left(\mathbf{r}\right)} + \gamma\frac{d}{d\gamma}v_c^\gamma \left([\rho];\mathbf{r}\right) - v_c^\gamma \left([\rho];\mathbf{r}\right) = 0,
$$

and therefore

$$
2\mu - 2\int d^3 r' v^\gamma \left([\rho];\mathbf{r}'\right) f^\gamma \left(\mathbf{r}'\right) - \int d^3 r' \mathbf{r}'.\nabla'v^\gamma \left([\rho];\mathbf{r}'\right) f^\gamma \left(\mathbf{r}'\right)
$$
$$
= \int d^3 r' \gamma\frac{\delta V_{ee}^\gamma [\rho]}{\delta\rho\left(\mathbf{r}'\right)} f^\gamma \left(\mathbf{r}'\right) \tag{39}
$$

The Fukui function is simply the difference between two densities[16]:

$$f_N^\gamma (\mathbf{r}') = \rho_N^1 (\mathbf{r}) - \rho_{N-1}^\gamma (\mathbf{r}). \tag{40}$$

Note that by construction only the $(N-1)$-electron density depends on γ. The external potential for the N and $(N-1)$ systems are the same, and hence the virial theorem[9] and Eq. (40) imply that,

$$\int d^3r' \mathbf{r}' . \nabla' v^\gamma \left(\left[\rho_N^1 \right]; \mathbf{r}' \right) f^\gamma (\mathbf{r}')$$
$$= 2T^\gamma \left[\rho_N^1 \right] + \gamma V_{ee}^\gamma \left[\rho_N^1 \right] - 2T^\gamma \left[\rho_{N-1}^\gamma \right] - \gamma V_{ee}^\gamma \left[\rho_{N-1}^\gamma \right]. \tag{41}$$

Combining (39), (41) and (32) leads to the main result of this paper:

$$V_{ee}^\gamma \left[\rho_N^1 \right] - V_{ee}^\gamma \left[\rho_{N-1}^\gamma \right]$$
$$= \int d^3r \frac{\delta V_{ee}^\gamma \left[\rho_N^1 \right]}{\delta \rho_N^1 (\mathbf{r})} \left(\rho_N^1 (\mathbf{r}) - \rho_{N-1}^\gamma (\mathbf{r}) \right). \tag{42}$$

III. COROLLARY: RECURSION RELATIONS

Recursion relations can be derived at coupling strength interaction γ, when the single particle external potential is kept fixed, i.e. for an M-electron system

$$\hat{v}_{\text{ext}}^M = \sum_{i=1}^{M} v_{\text{ext}}^\gamma \left(\left[\rho_N^1 \right]; \mathbf{r}_i \right). \tag{43}$$

and $\rho_M^\gamma \equiv \rho_M^\gamma (v_{\text{ext}}^\gamma [\rho_N^1])$ is the M-electron density constructed from a groundstate of the M-electron Hamiltonian $\hat{H}_M^\gamma = \hat{T}^M + \gamma \hat{V}_{ee}^M + \hat{v}_{M,\text{ext}}^\gamma [\rho_N]$. The potential $\hat{v}_{N,\text{ext}}^1 [\rho_N]$ for a real system is the interaction potential between electrons and nuclei. From Eq. (42),

$$V_{ee}^\gamma \left[\rho_N^1 \right] - V_{ee}^\gamma \left[\rho_{N-1}^\gamma \right]$$
$$= \int d^3r \frac{\delta V_{ee}^1 \left[\rho_N \right]}{\delta \rho_N^\gamma (\mathbf{r})} \left(\rho_N^1 (\mathbf{r}) - \rho_{N-1}^\gamma (\mathbf{r}) \right) \tag{44}$$

and

$$V_{ee}^\gamma \left[\rho_{N-1}^\gamma \right] - V_{ee}^\gamma \left[\rho_{N-2}^\gamma \right]$$
$$= \int d^3r \frac{\delta V_{ee}^\gamma \left[\rho_{N-1}^\gamma \right]}{\delta \rho_{N-1}^\gamma (\mathbf{r})} \left(\rho_{N-1}^\gamma (\mathbf{r}) - \rho_{N-2}^\gamma (\mathbf{r}) \right). \tag{45}$$

Continuing this pattern leads to

$$
\begin{aligned}
& V_{ee}^{\gamma}\left[\rho_N^{\gamma}\right] - V_{ee}^{\gamma}\left[\rho_{N-M}^{\gamma}\right] \\
& = \sum_{L=0}^{N-1} \int d^3r \frac{\delta V_{ee}^{\gamma}\left[\rho_{N-L}^{\gamma}\right]}{\delta \rho_{N-L}^{\gamma}(\mathbf{r})}\left(\rho_{N-L}^{\gamma}(\mathbf{r}) - \rho_{N-1-L}^{\gamma}(\mathbf{r})\right),
\end{aligned} \tag{46}
$$

and since $V_{ee}^{\gamma}\left[\rho_1^{\gamma}\right] = 0$, it follows that,

$$
V_{ee}^{\gamma}\left[\rho_N^{\gamma}\right] = \sum_{L=0}^{N-2} \int d^3r \frac{\delta V_{ee}^{\gamma}\left[\rho_{N-L}\right]}{\delta \rho_{N-L}^{\gamma}(\mathbf{r})}\left(\rho_{N-L}^{\gamma}(\mathbf{r}) - \rho_{N-1-L}^{\gamma}(\mathbf{r})\right). \tag{47}
$$

IV.   DISCUSSION AND SUMMARY

For $\gamma = 0$, $V_{ee}^0[\rho] = E_x[\rho] + U[\rho]$[11,12]. From Eq. (42) then follows the equation

$$
E_x\left[\rho_N^1\right] + U\left[\rho_N^1\right] - E_x\left[\rho_{N-1}^0\right] - U\left[\rho_{N-1}^0\right] = \int d^3r \frac{\delta\left(E_x\left[\rho_N^1\right] + U\left[\rho_N^1\right]\right)}{\delta \rho_N^1(\mathbf{r})}\left(\rho_N^1(\mathbf{r}) - \rho_{N-1}^0(\mathbf{r})\right)
$$

or

$$
\begin{aligned}
& E_x\left[\rho_N^1\right] - E_x\left[\rho_{N-1}^0\right] \\
& = \int d^3r \frac{\delta\left(E_x\left[\rho_N^1\right]\right)}{\delta \rho_N^1(\mathbf{r})}\left(\rho_N^1(\mathbf{r}) - \rho_{N-1}^0(\mathbf{r})\right) \\
& + \frac{1}{2}\int d^3r\,d^3r'\left(\rho_N^1(\mathbf{r}) - \rho_{N-1}^0(\mathbf{r})\right)\frac{1}{|\mathbf{r} - \mathbf{r}'|}\left(\rho_N^1(\mathbf{r}') - \rho_{N-1}^0(\mathbf{r}')\right).
\end{aligned} \tag{48}
$$

This expression has already been derived by Levy and Görling[19]. The relation derived here, Eq. (42), is generalization of their work, valid at all coupling strengths. Note that in the derivation of Eq. (3) use is made of Eq. (11), (30) and (31). This implies that derivation is correct for v-representable densities[11,12] and the question whether it is correct for general densities remains.

In summary, a relationship between the Coulomb interaction functionals of a many electron system at charge densities that differ by one electron, evaluated at the same external potential, was derived. The derivation was done for integer numbers of particles, but can be extended to fractional particle numbers. As a corollary, it was shown that the Coulomb interaction functional can be expressed as a sum over integrals of functional derivatives of the Coulomb interaction functionals and charge densities for all densities that differ form the total density by an integer. These relations place stringent constraints on the energy functionals that appear in density functional theory and it will be difficult for approximate functionals to satisfy these equations.

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